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AN OVERVIEW OF THE BIODEGRADATION OF CHLORINATED HYDROCARBONS

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AN OVERVIEW OF THE BIODEGRADATION OF CHLORINATED HYDROCARBONS

by

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INTRODUCTION

A major reason for the increasing environmental importance of many chlorinated hydrocarbons is their apparent recalcitrance to microbial attack. Compounds which are not broken down by microorganisms accumulate in soil and natural waters and, consequently, in plants and animals. The following pages contain an overview of research carried out, mainly from 1970 - 1983, on the microbial degradation of a number of chlorinated hydrocarbons (selected by Environment Canada).

In general, biodegradation of chlorinated hydrocarbons is dependent on their chemical structure and on environmental conditions. The position of the chlorine affects the decomposition pattern. Ring substitution and the nature of aliphatic side chains determine the susceptibility of the aromatic compounds to microbial decomposition.

It is well known that environmental properties such as pH, temperature, and moisture will greatly influence the fate of a chemical compound in nature, especially in soil. The extent of persistence depends upon: (1) chemical properties of the compound, (2) physical, chemical, and biological properties of the soil, (3) climatic conditions (cf. Fig. 1, p. 58). For many potential environmental pollutants the degree of persistence will depend to a large extent on the biochemical versatility of soil microbial populations. Among soil bacteria, Pseudomonas spp. have evolved considerable nutritional versatility.

Recent studies have shown that members of the genus Alcaligenes can degrade a variety of synthetic chlorinated aromatic and aliphatic compounds, with the aid of naturally-occurring plasmids. As the following pages show, a number of other microorganisms have also been implicated in the breakdown of chlorinated hydrocarbons.

Chlorinated hydrocarbons added to soil may influence each other's fate. Low concentrations of a number of such compounds interfere with the degradation of an added second compound. On the other hand, there may be a more rapid breakdown of a chlorinated hydrocarbon in soil previously treated with the same hydrocarbon, or an analog.

In the following text, the figures, tables, and references are given for each compound or group of compounds separately for easier access. Details of the literature search profile and a complete list of the obtained references, on which this overview is based, are filed with Environment Canada.

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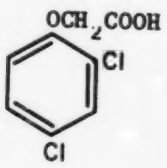
PHENOXYACETATES

2,4-D and MCPA

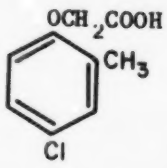
Both 2,4-D (2,4-dichlorophenoxyacetic acid) and MCPA (4-chloro-2-methyl-phenoxy-acetic acid) are chlorophenoxyacetic herbicides.

Phenoxyacetates are formed by attaching various substituents to phenoxy carboxylic acids.

2,4 D



MCPA



The phenoxyacetic herbicides are commercially available as free acids, amines, salts and esters. Their application rates vary according to crop, species area (cropland, brushland, lakes), etc. Average applications are about 0.8 kg/ha of 2,4-D on cropland and pasture in Canada. Higher amounts are used on brushland (4-6 kg/ha). Applications to lakes and ponds may be 22-45 kg/ha (NRCC, 1978).

Since their discovery in 1942 the phenoxy herbicides have remained the most important herbicides in weed control (Loos, 1975). They are also the most used herbicides in the world.

After application, herbicides are exposed to various degradation processes (chemical, photochemical and biological). Certain transformations in phenoxy herbicides can occur as chemical or photochemical processes, although complete degradation is only performed by biological processes. Numerous higher plants are able to degrade phenoxy herbicides. Microorganisms which

can degrade 2,4-D and MCPA are naturally present in soil and water. These compounds are among the few herbicides that some bacteria can use as the sole source of carbon and energy (Kilpi, 1980).

Numerous investigations have confirmed that phenoxy herbicides, applied at suggested rates, disappear quickly and do not accumulate in the environment (Wilson and Cheng, 1978; Jenkins et al., 1978; Liu et al., 1981). Only rarely do low concentrations of residues remain after herbicide disappearance, and these do not appear to be toxic for microorganisms. Under normal field conditions the breakdown rates of 2,4-D and MCPA may be similar, although 2,4-D appears to be less persistent. Residues from normal agricultural applications of these two compounds are usually degraded within a few weeks to a few months, and are not expected to be carried over from one growing season to the next. Carry-over would only be a problem in very cold, dry, or acidic soils, or in other extreme conditions.

Currently, there is more known about the effect of 2,4-D on soil microflora than of any other herbicide. Facultative anaerobes are more tolerant to high concentrations than other microorganisms. Phenoxy herbicides are more toxic in acid than in alkaline soils. Studies on microorganisms exposed to high levels of phenoxy herbicides in soil have shown that the massive applications did not sterilize the soil but stimulated part of the microflora able to degrade the added herbicide. Many observations were made of a lag period after the first application of herbicide, during which no appreciable changes in herbicide concentration occur (Kaufman and Kearney, 1976). There seems to be an adaptation period that is followed by rapid herbicide degradation. Subsequent additions always disappear without a lag period (Kaufman

and Kearney, 1976). This degradation ability can persist over a long period without the compound being present. There is a "cross adaptation" pattern in soil, which allows a rapid degradation of 2,4-D in MCPA-enriched soils and vice versa.

Phenoxy herbicides are mostly degraded aerobically by mixed microbial soil cultures (Loos et al., 1979). That the compounds are also degraded by co-metabolism is known, but it has been difficult to demonstrate in nature. Recent studies with ^{14}C-labeled herbicides in soil and in sludge have provided the evidence for the existence of co-metabolism.

A number of soil microorganisms are able to degrade the phenoxy herbicides through several pathways. Most of the information about these metabolic pathways has been obtained with bacterial cultures isolated from soil (Table 1). Fig. 1 shows a pathway for the metabolism of 2,4-D (Munnecke et al., 1982). A similar pathway exists for MCPA degradation (with a 2-methyl substitution for 2-Cl) (Loos, 1975). The pathways have been established by studies with Pseudomonas and Arthrobacter spp. The acids produced by these degradations can be metabolized further by the tricarboxylic acid cycle. There is evidence of other possible pathways from studies with Pseudomonas spp. (Fig. 2).

In nature, when dealing with mixed cultures, it is not essential that one single organism be able to degrade the pesticide alone. There are numerous breakdown products from phenoxy herbicides, which may accumulate during decomposition, although many investigations have shown that the final products are carbon dioxide, chlorine and water. In soil, microorganisms are always competing for degradable compounds. Furthermore, a number of soil microorganisms have remarkable adaptive power and some of them can alter their metabolic pathways to utilize different compounds.

The first important step in the degradation of 2,4-D and MCPA involves their transformation into corresponding phenols with removal of the acetic acid side chain. After hydroxylation to produce a catechol the next important step, ortho or meta cleavage, can be accomplished by many microorganisms (Fig. 3) (Kilpi et al., 1980). During degradation of MCPA, chloride was liberated after the ring fission, while for 2,4-D, one of the chlorides could be released before (Evans et al., 1971). The resistance to ring cleavage of MCPA has been reported to be greater than that of 2,4-D by some workers; others have found the opposite result, but in any case, the differences are small. In another degradation study, the cleavage of chlorides started simultaneously for both MCPA and 2,4-D. Overall, 2,4-D seems more susceptible to microbial attack.

Under optimal conditions of moisture and temperature, microbial populations will be supported in their degradation of herbicides. Usually, in a soil with high organic content, an increased rate of herbicide degradation has also been observed (McCall et al., 1981). The degradation of phenoxyacetic herbicides decreases with increasing depth in soil. pH has a marked effect (Sattar and Paasivirta, 1980). With low pH values, the degradation rate of MCPA falls off faster than that of 2,4-D. In acid soils (pH 3.5-5.0) MCPA was degraded within 5-9 weeks, but in neutral soil (pH above 6.3) degradation required only one week.

The evolution and spread of pesticide-degrading plasmids in microorganisms plays a major role in the widespread occurrence of microbial populations capable of degrading certain environmental pollutants (Farrell and Chakrabarty, 1979). For 2,4-D and MCPA degradation, part or all of the information for the degradation pathway is carried on conjugative plasmids in Alcaligenes eutrophus and A. paradoxus (Don and Pemberton, 1981). A ready

transfer of 2,4-D degrading plasmids within Alcaligenes spp. suggests that soilborn organisms of this genus play a major role in degrading and recycling a number of chlorinated compounds related to 2,4-D and MCPA in the environment. Some of the 2,4-D degrading plasmids are of major interest as they confer on bacteria the ability to degrade m-chlorobenzoate (Fisher et al., 1978).

In conclusion, 2,4-D has been found to be the most studied herbicide. Following adaptation of microbial populations, MCPA and 2,4-D disappear quickly from soil under favorable growth conditions. Apart from plant metabolism, volatilization, chemical and photochemical degradation, microbial degradation is the most important process for the removal of phenoxy herbicides in nature. Bacteria are able to degrade these compounds completely, in relatively short periods of time.

Factors that favor growth of aerobic microorganisms, mixed microbial populations and co-metabolism will also favor degradation of phenoxy herbicides in nature. Such factors include high moisture content, moderately high temperatures, aerobic conditions, nutrients, and high organic matter content.

Table 1

Organisms that degrade phenoxyacetic acids

(After Loos, 1975).

	2,4-D	MCPA	
Flavobacterium peregrinum	+	+	
Corynebacterium sp.	+		
Corynebacterium - like organism	+	+	
Achromobacter sp.	+	+	
Sporocytophaga congreta	+		
Arthrobacter globiformis	+		
Arthrobacter sp.	+	+	
Pseudomonas sp.	+	+	
P. subcreta - *P. pictorum*	+	+	
Nocardia sp.	+		
Streptomyces viridichromogenes	+		
Alcaligenes eutrophus	+	+	(Don and Pemberton, 1981)
Alcaligenes paradoxus	+	+	(Don and Pemberton, 1981)

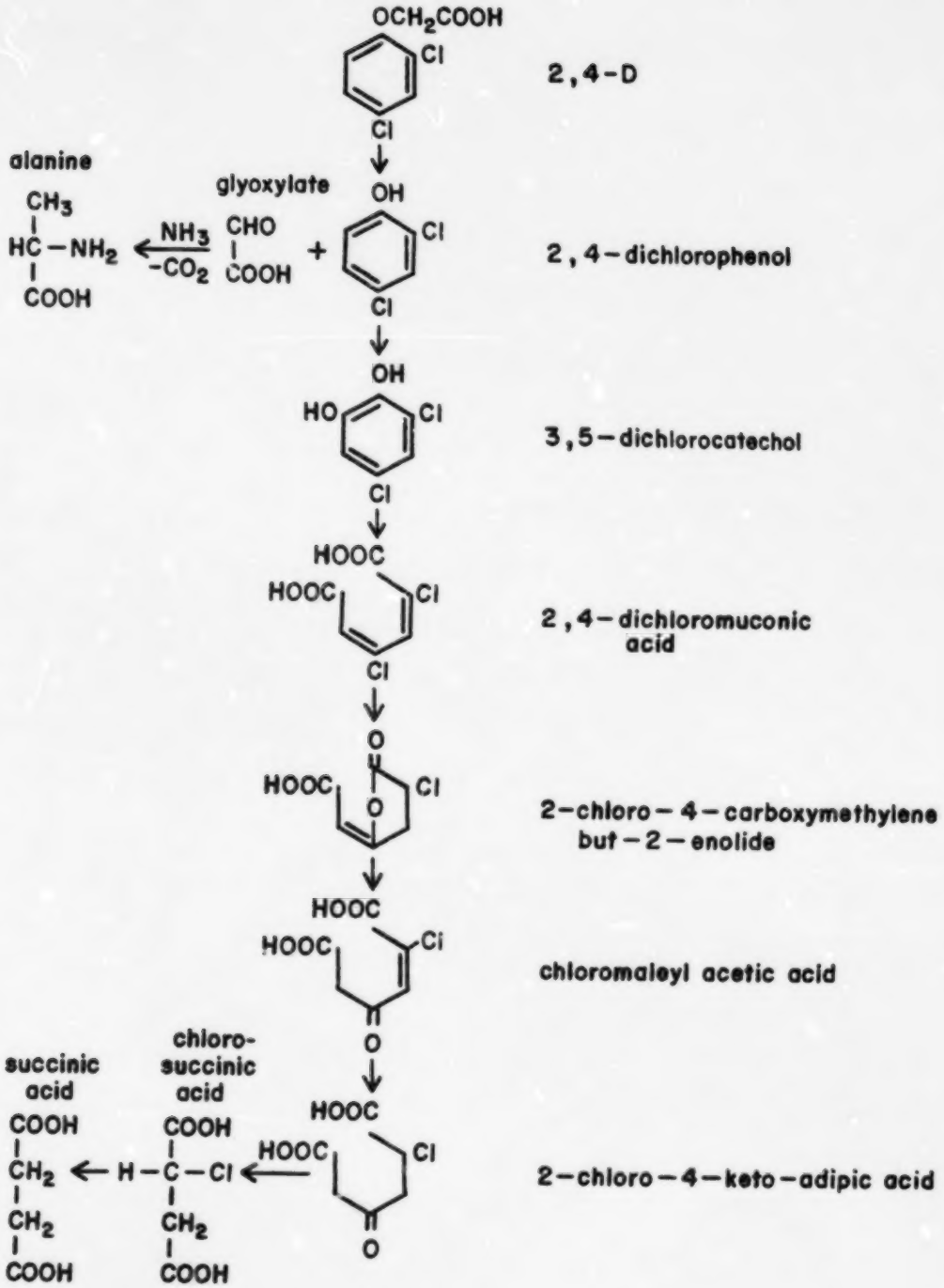


Fig. 1. Pathway for microbial degradation of 2,4-D.

(After Munnecke et al., 1982).

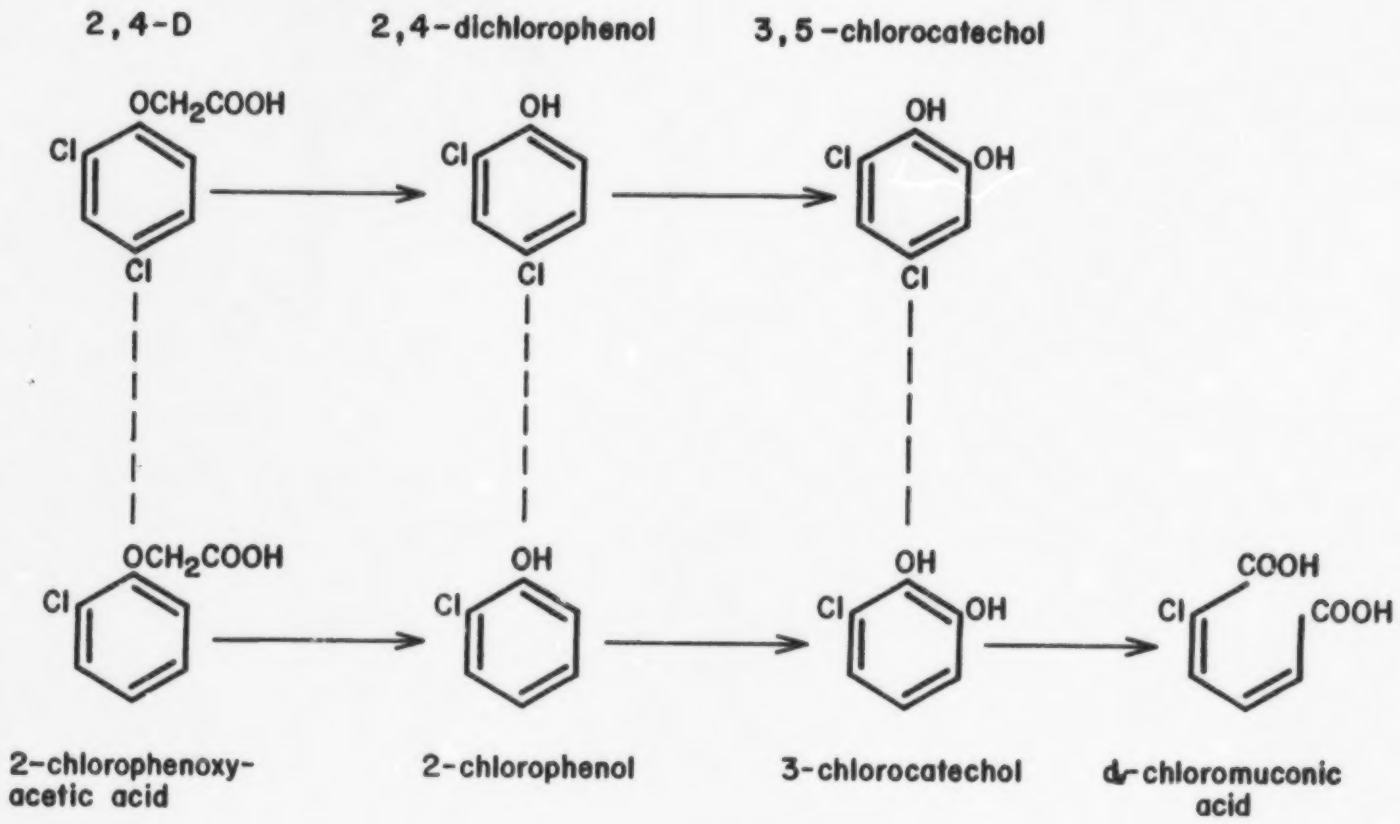


Fig. 2. Possible pathways of 2,4-D degradation.
(After Evans et al., 1971; Loos, 1975).

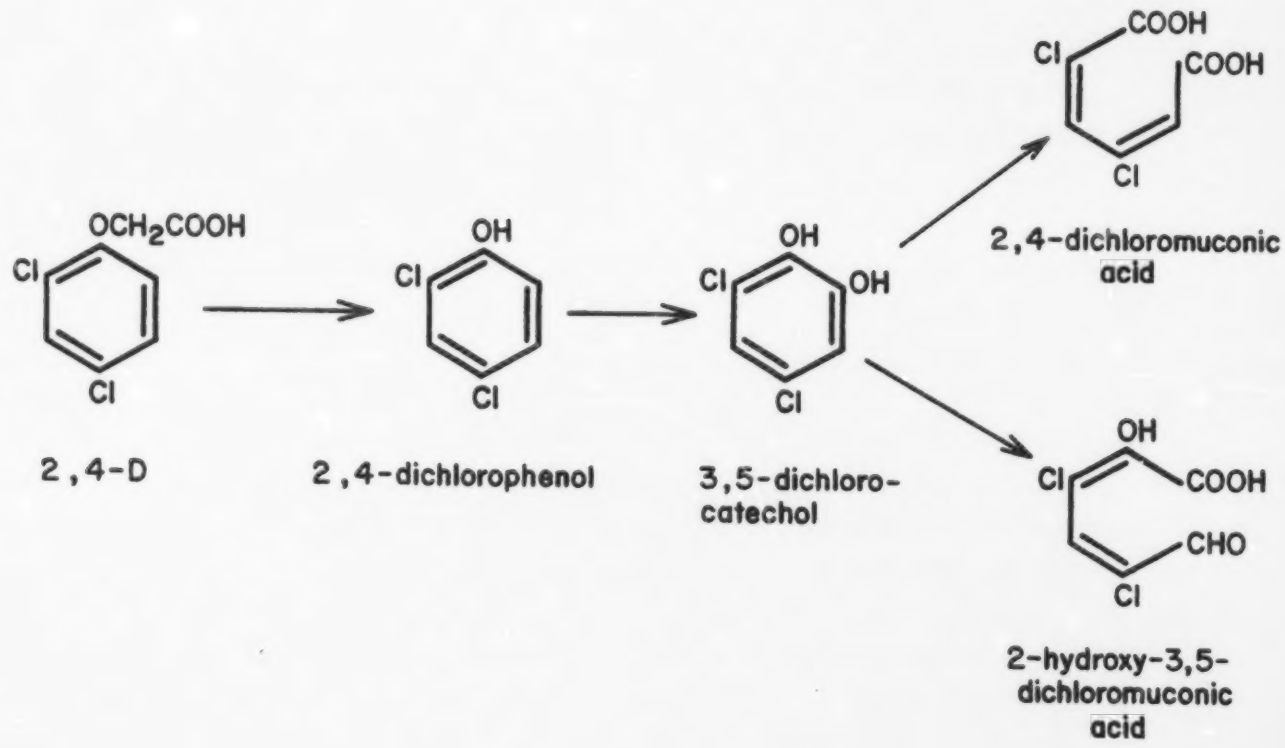


Fig. 3. Proposed pathway of 2,4-D degradation.
(After Kilpi et al., 1980).

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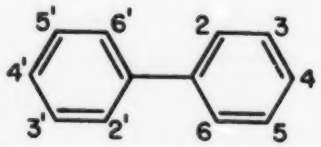
POLYCHLORINATED BIPHENYLS

Polychlorinated biphenyls (PCBs) are a group of chlorinated hydrocarbons commercially produced by chlorination of biphenyl in the presence of a suitable catalyst.



The chlorination of biphenyl can lead to replacement of hydrogen atoms by chlorine in ten positions. The conventional numbering is shown in the above diagram.

The number of chlorine substitutions on the biphenyl molecule corresponds to the chemical nomenclatures:

monochlorobiphenyl	2-chlorobiphenyl
	4-chlorobiphenyl
dichlorobiphenyl	2,4'-dichlorobiphenyl
trichlorobiphenyl	3,4,4'-trichlorobiphenyl

etc.

The PCBs are known by a variety of trade names, Aroclor (USA), Kanechlor (Japan), Phenochlor (France), Fenchlor (Italy), Clophen (FRG), Sovol (USSR). Each PCB product is a mixture of chlorobiphenyls (Fishbein, 1972). Most information is available for the Aroclor products, which are characterized by four-digit codes. The first two digits refer to the type of molecule (12 - biphenyls) (Brinkman and de Kok, 1980). The last two digits give the weight percent of chlorine in the final mixture. Aroclor 1248 is a polychlorinated biphenyl mixture with 48% of chlorine, while Aroclor 1221 contains only 21% chlorine. Several investigations have been made on commercial products to identify individual PCBs in the mixtures (Table 1). Also, individual PCBs

have been synthesized for identification purposes, for toxicological investigations and degradation studies (Sundström et al., 1976).

The outstanding physical and chemical properties of PCBs have made them very useful as lubricants, plasticizers, flame retardants, dielectric fluids, and heat transfer agents. The PCBs are resistant to oxidation, acids, bases and other corrosive agents; they are insoluble in water, soluble in organic compounds and they have excellent dielectric properties. The same properties which led to their extensive use have also led to their accumulation in the environment (Kimbrough, 1980; Mackay et al. 1983). The polychlorinated biphenyls have been widely used in industry since 1930, and in 1966 Jensen first reported PCBs as environmental contaminants because of their persistence and bioaccumulation in food chains. The problem has now been well documented; thus, biota, atmosphere, soil, water and sediments are found to be contaminated. The pollution of the environment has occurred from leaks and disposal of industrial fluids, vaporization from plasticizers, disposal in dumps and landfills, and sewage sludge disposal onto fields. Severe contaminations have occurred - the Hudson River contamination with effluents from General Electric plants, fish meal contamination at a Ralston Purina plant, rice oil contamination in Japan (Kuratsune, 1980).

Disposal sites represent a local contamination problem. Although they are sizable reservoirs of PCBs, little is known of their fate during long residence periods (Miller, 1982). The investigations of the Hudson River area indicate negligible groundwater contamination by PCBs. It was shown experimentally that PCBs are not leached from soil by percolating water or land fill leachate, especially higher chlorinated PCBs, which are preferen-

tially adsorbed by soil materials. Those with lower chlorination are removed slowly, particularly from soils with high clay content. It is difficult to predict the effective rate of release of PCBs, as the composition of PCBs in the disposal site, as well as soil properties, weathering and probable biodegradation affect the fate of PCBs. There is relatively little quantitative information on the rate at which PCBs are declining in the environment. The low chemical and metabolic reactivity of PCBs make them persistent pollutants. As they are rather fat- than water-soluble, they accumulate in organisms high in the food chain and therefore can be toxic (NRCC, 1978). Several investigations show a possible metabolism of PCBs by animals, birds, fish, although the extent may be very low (Sundström et al., 1976).

Natural microbial communities appear to respond to environmental pollutants by developing detoxification processes which may be very slow at first. There has recently been some evidence that microorganisms are able to modify their degradation pathways to metabolize some highly chlorinated compounds (Bédard et al., 1984). Still, highly chlorinated PCBs (those containing 4 to 5 or more chlorine atoms per biphenyl molecule) are not known to be degraded by the soil microflora to any significant extent (Parson et al., 1983). As many different enzymes are needed to degrade a toxic compound, many different microorganisms can contribute. If one link is missing in the conversion, some metabolites or intermediates tend to accumulate. Also cometabolism, that is, partial degradation of a compound by microorganisms that cannot use it as a carbon source, is known to be important in chlorobiphenyl degradation.

Biodegradation is the most important process for complete removal of

environmental pollutants, although persistent compounds, by definition, are not easily degraded by microorganisms. Only a few members of the microbial population harbor the special abilities to degrade chlorinated hydrocarbons. Some of the bacteria, reported capable of degrading polychlorinated biphenyls, are listed in Table 2. PCBs are degraded mainly by gram negative bacteria isolated from soil. In addition, a few of the gram positive bacteria are found among the degraders, including Nocardia, Arthrobacter and Corynebacterium. The degradation of various chlorinated hydrocarbons is often associated with occurrence of plasmids, and the evolution of plasmids encoding bioconversion is the main factor for biodegradation of chlorobiphenyls. Mixed cultures of bacteria, harboring different plasmids, are often better able to degrade PCBs than individual strains. Chakrabarty (1982) reported that a mixed culture of two bacteria (Acinetobacter strain P6; Pseudomonas putida) growing on chlorobiphenyls as sole sources of carbon was able to degrade them completely (>90%) with a release of Cl^-. The interaction of two degradative plasmids led to total destruction of persistent compounds such as 4-chlorobiphenyl and 3,5-dichlorobiphenyl. Furusaka and Chakrabarty (1982) reported on a novel replication of such plasmids in both gram negative and gram positive bacteria.

To understand the effect and influence of mixtures of PCBs, in nature, it is important to understand the biodegradability pattern of each chemical component in the mixture, and their combined degradability. It is well known that increase of chlorine atoms per biphenyl molecule increases the resistance to biodegradation. How the chlorines are distributed between the two benzene rings is important. Microorganisms preferentially degrade the less chlorinated of the two. The initial attack is on the one with no or with few chlorine atoms. The position of chlorine substituents on the biphenyl mole-

cule is important for PCB degradation. In both pure and mixed cultures of bacteria mono- and dichloro biphenyls are degraded to some extent, while there are very few reports on the degradation of the highly chlorinated biphenyls. Achromobacter isolated from sewage sludge degraded mono- and dichloro biphenyls (Ahmed and Focht, 1973). Several low chlorine PCBs were more readily degraded by Nocardia sp. and Pseudomonas sp. than were the higher chlorinated compounds (Baxter et al., 1975). Mixed cultures of bacteria, predominantly Alcaligenes odorans, Alcaligenes denitrificans, and an unidentified bacterium, degraded the lower chlorinated biphenyls in Aroclor 1242 at a faster rate and also utilized them more completely than those that had higher chlorination (Clark et al., 1979).

As commercial PCBs are not a single entity but a complex mixture, the different components undergo biological degradation at different rates. Many investigations have shown that the level of chlorination is an important factor in determining PCBs relative persistence to biodegradation under natural conditions. Tucker et al. (1975) demonstrated differences in biodegradation rates of commercial PCBs: mixtures with mono- and dichlorobiphenyls readily undergo degradation by activated sludge microorganisms but the rates decrease as the levels of chlorination increase (Figure 1). A degradation study of a polychlorinated biphenyl-containing dielectric fluid waste, with a mixed population of bacteria isolated from sewage sludge, showed degradation of the mono- and dichlorinated compounds within 4 days but no degradation of more chlorinated compounds was observed after 2 months incubation (Quirk, 1983). In the same investigation there was no evidence of

degradation in sealed flasks, i.e., under anaerobic conditions. It is known that molecular oxygen is needed for biodegradation of hydrocarbons. In general, research on anaerobic environments has not shown any evidence of PCB degradation. However, recent research on chlorinated aromatic compounds indicates that some anaerobic degradation could occur, namely dechlorination (Suflita et al., 1983). Some investigations report on degradation and others on no degradation with activated sludge treatment of waters containing PCBs.

Several reviews have recently dealt with microbial degradation of chlorobiphenyls (Furukawa, 1982; Parsons et al., 1983). A microbial degradation of PCBs is illustrated in Figure 2. Possible routes for PCB degradation have been suggested from studies with microbial breakdown of aromatic hydrocarbons.

Photolysis by sunlight could also be important for the degradation process, as photolysis converts highly chlorinated into less chlorinated PCBs (NRCC, 1978). Since microbial degradation of PCBs increases as chlorine substitution decreases, a combination of photolysis and microbial degradation should work well to decrease both high and low chlorinated PCBs in the environment. On the other hand, most PCBs in the environment are not exposed to sunlight, e.g. in soil and sediment, and therefore photodegradation is likely to play a minor role.

Most of the reported experimental work has been done in laboratory systems with optimal conditions. It is difficult to predict how microbial cultures will react in an environment with varying parameters and in competition with the existing microflora. Also, extrapolating the biodegradation rates from laboratory systems to different environments is extremely difficult.

There is little evidence for accumulation of intermediates from PCB biodegradation. If "partial biodegradation" of a PCB mixture does occur, it usually means that some components are completely degraded, some partially, and others not at all. Complex biodegradation mechanisms are involved, and this raises the possiblity that new, and perhaps more toxic, intermediates are formed. Thus, caution should be taken when laboratory experimental results based on pure substrate and culture studies are used to predict the fate of a commercial PCB in the environment. It is unlikely that meaningful predictions, can be made from pure culture studies alone.

Polybac Corporation has developed mutant bacteria products capable of destroying chemicals in soil. Polybac has one product for degrading polychlorinated biphenyls, which works efficiently on less chlorinated biphenyls (Environmental Protection Service, 1983).

Table 1.
Approximate percent composition of Aroclors

(After Brinkman and de Kok, 1980)

Chlorobiphenyl	No. of Cl atoms/biphenyl	Aroclor 1221	1232	1016 a)	1242	1248	1254	1260
$C_{12}H_{10}$	0	10						
$C_{12}H_9Cl$	1	50	26	2	1			
$C_{12}H_8Cl_2$	2	35	29	19	13	1		
$C_{12}H_7Cl_3$	3	4	24	57	45	21	1	
$C_{12}H_6Cl_4$	4	1	15	22	31	49	15	
$C_{12}H_5Cl_5$	5				10	27	53	12
$C_{12}H_4Cl_6$	6					2	26	42
$C_{12}H_3Cl_7$	7						4	38
$C_{12}H_2Cl_8$	8							7
$C_{12}H\ Cl_9$	9							1

a)
Aroclor 1016 is a distillation product of Aroclor 1242 containing only 1% of components with five or more chlorine atoms.

Table 2. PCB-degrading bacteria used in degradation experiments.

Achromobacter pCB		Ahmed and Focht, 1973
Pseudomonas sp.		Baxter et al., 1975
Nocardia sp.		" "
Pseudomonas sp.		Sayler et al., 1977
Pseudomonas sp. 7509		Liu, 1980
Alcaligenes sp. Y42		Furukawa and Matsumura, 1976
Acinetobacter sp. P6		Furukawa et al., 1978
Alcaligenes odorans *Alcaligenes denitrificans* an unidentified bacterium	mixed cultures	Clark et al., 1979
Alcaligenes eutrophus H850		Bedard et al., 1984
Corynebacterium sp. MB1		" "
Klebsiella pneumoniae AC901		Kamp and Chakrabarty, 1979

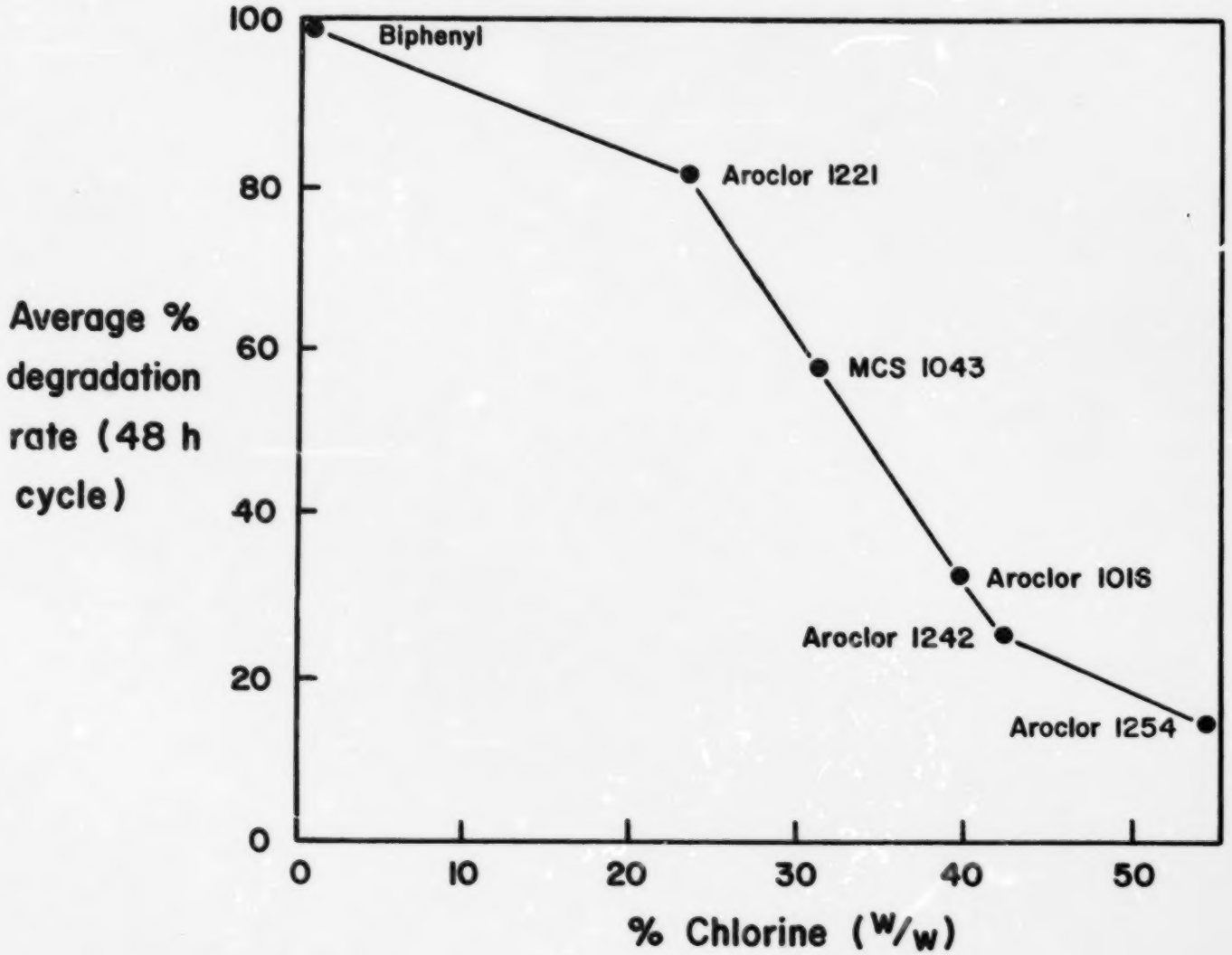


Fig. 1. Semi-continuous activated sludge degradation of commercial PCBs as a function of the weight percent chlorine. Addition rate, 1 mg/48 h. (After Tucker et al., 1975).

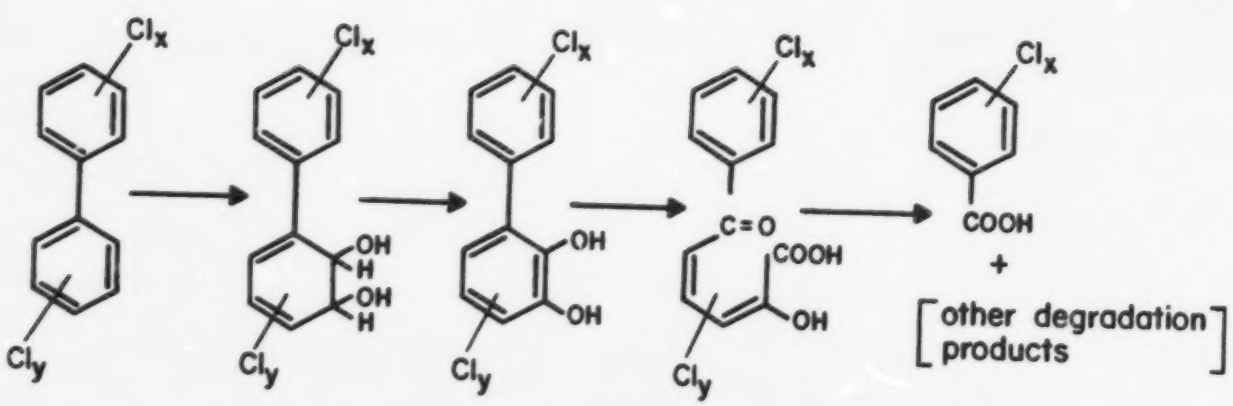


Fig. 2. Principal pathway for microbial degradation of PCBs.
(After Furukawa et al., 1979; Parson et al., 1983).

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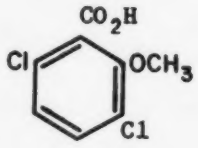
DICAMBA

(2-methoxy-3,6-dichlorobenzoic acid)

Dicamba (2-methoxy-3,6-dichlorobenzoic acid) is used as post-emergence herbicide for the selective control of weeds on small grains, pasture lands and turf grass and for certain types of brush control. Dicamba is used as the free acid or its salts. Dicamba is a haloaromatic compound and is chemically relatively inert (stable to oxidation and hydrolysis)



MW

221.0

The few studies on dicamba show that it is readily degraded in soil. The degradation is considered to be of microbial origin. Both soil moisture and aeration enhance the degradation of dicamba. Evidence for a rapid microbial degradation of dicamba in Canadian prairie soils was provided by Smith (1973).

In a degradation study of dicamba in different soils (silty clay, heavy clay, sandy loam) both gas chromatographic and radiochemical analytical techniques were used (Smith, 1974). In all three soils the herbicide disappeared within three weeks, as shown by ^{14}C-ring-labeled dicamba. During dicamba degradation an accumulation of a metabolite occurred. The only degradation products detected were carbon dioxide and 3,6-dichlorosalicylic acid. The formation of 3,6-dichlorosalicylic acid appeared to be greatest in the silty clay. After the initial build-up the metabolite was slowly degraded. In all three soils an almost complete degradation was observed within 9 weeks. It seems that 3,6-dichlorosalicylic acid is much more strongly absorbed onto various soils than dicamba.

Altom and Stritzke (1973) observed a rapid disappearance of dicamba in soils during the first 20 days of incubation in growth chambers. The degradation rate was higher for grassland soil than for forest soils as the calculated half life for dicamba was 17 days in grassland soil and 26 to 32 in forest soils.

It is evident that favorable environmental conditions, which increase microbial activity in soils, increase degradation of dicamba.

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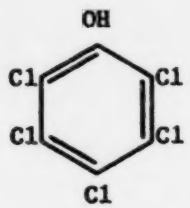
PENTACHLOROPHENOL

PCP



Pentachlorophenol (PCP) has many applications (e.g., bactericide, algicide, fungicide, insecticide, and herbicide). The most important use of PCP is for wood preservation, mainly as a fungicide. It is also used as a fungicide for slime control in manufacturing a variety of products such as paper, leather, and paint. It has been used most extensively as a herbicide in rice paddy fields.

Commercial pentachlorophenol marketed in Canada (Uniroyal Ltd., Clover Bar, Alta) is produced by catalytic chlorination of phenol (Baker and Matheson, 1981). Commercial PCP contains significant quantities of other isomers (tetrachlorophenol, trichlorophenol) as well as smaller quantities of other impurities (e.g., dioxins). Those impurities are extremely important in environmental toxicity. For example, dioxins are toxic, persistent compouuds and their introduction into the environment can lead to both accumulation and biological magnification.

This overview indicates that pentachlorophenol does not persist in soil. It disappears by volatilization, degradation, uptake of residues by plants and incorporation of residues into soil constituents. The initial degradation of pentachlorophenol in soil seems to occur primarily by dehalo-

genation but methylation of PCP to pentachloroanisole also has been observed (Weiss et al., 1982). The further breakdown of PCP has been shown to involve partially dechlorinated hydroquinone intermediates, which then undergo ring cleavage.

A number of studies have reported the breakdown of PCP and related compounds by pure or mixed cultures of bacteria and by fungi (Kaufman, 1978; Reiner et al., 1978). Several degradation pathways have been identified. PCP may be subjected to methylation, reductive or oxidative dehalogenation and ring cleavage. Although methylation reduces the toxic effects of chlorophenols, the methylation product of PCP, pentachloroanisol (PCA), appears to be more persistent than PCP. Chlorophenols are reported as intermediates in the microbial degradation of PCP (dehalogenation). Baker and Mayfield (1980) studied degradation of various chlorophenols by soil microorganisms. Under aerobic conditions several lower chlorinated phenols were rapidly degraded while others (m-chlorophenol, 3,4-dichlorophenol, 2,4,5-trichlorophenol) were degraded at the same slow rate as pentachlorophenol. It seems that 3,4,5-trichlorophenol and 2,3,4,5-tetrachlorophenol were not readily susceptible to microbial degradation.

Numerous factors affect the degradation of pentachlorophenols in soil (e.g., soil type, pH, organic matter content, aeration, moisture content, and temperature). Soils with high organic matter content degraded PCP better than soils with low organic contents. PCP disappeared more rapidly under anaerobic conditions than under aerobic conditions in different rice paddy soils (Kuwatsuka and Igarashi, 1975). An adaptation period of the compound to microbiological degradation has been observed and repeated applications of PCP has caused accelerated degradation in paddy fields. An acclimation process of aerobic microflora to PCP is also well documented. A more rapid

degradation occurred when the temperature approached the optimum temperature of microbial activity in soil.

To maintain the highest microbial degradation possible pH should be kept high as the effect of low pH on PCP toxicity has been shown for both bacteria and fungi. Complete PCP degradation is also reported to be most effective under aerobic conditions. After 160 days of incubation of PCP in soil under aerobic and anaerobic conditions, 80% and 7% of PCP was degraded, respectively (Baker and Mayfield, 1980). Stanlake and Finn (1982) concluded that bacterial mineralization of PCP occurs only aerobically. These conclusions disagree with the work of Kuwatsuka and Igarashi (1975). This could have depended on the differences in the ecosystems studied (established PCP degrading anaerobic population vs. aerobic population).

Static-culture-flask biodegradation screening test studies showed that pentachlorophenol was significantly degraded by wastewater microbiota (Tabak et al., 1981). These studies showed that to achieve "100% biodegradation" (actually 90%), an adaptation to pentachlorophenol occurred, which was dependent on the substrate concentration. There was a gradual adaptation process over a 2-week period for 5 mg/l pentachlorophenol cultures and over a 4-week period for 10 mg/l cultures.

As conventional activated sludge treatment of wastewaters containing PCP have been shown to be ineffective and unreliable, some attempt have been made in recent years to improve the system for certain industries. Edgehill and Finn (1982) reported on an activated sludge treatment of synthetic wastewater containing pentachlorophenol. They described the response to a PCP shock load (from 40 to 120 mg/l of PCP) which upset the system of acclimated sludge for two days. Under the same conditions the shock loading effects were considerably improved when a chemostat culture of PCP-metabolizing Arthrobacter

was slowly added to the mixed liquor tank. In a short time (18 h instead of two days) the system returned to near steady-state conditions. Direct inoculation of Arthrobacter into PCP- contaminated soil was also shown to be an effective way to increase the PCP disappearance (Edgehill and Finn, 1983).

Only a limited number of bacterial isolates reported in the literature can use PCP as a sole carbon and energy source. Also, bacteria able to mineralize PCP are susceptible to PCP toxicity. The length of the lag period before PCP mineralization has been observed is directly proportional to the PCP concentration.

Reported PCP degrading bacteria are:

Corynebacterium	KC-3	Chu and Kirsch, 1972
Pseudomonas sp.		Suzuki, 1977
Arthrobacter sp.		Edgehill and Finn, 1982

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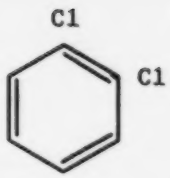
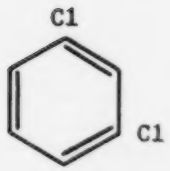
DICHLOROBENZENE

$C_6H_4Cl_2$





ortho-dichlorobenzene	meta-dichlorobenzene	para-dichlorobenzene
o-dichlorobenzene	m-dichlorobenzene	p-dichlorobenzene
1,2-dichlorobenzene	1,3-dichlorobenzene	1,4-dichlorobenzene

Dichlorobenzenes can be produced by chlorination of benzene or chlorobenzene at 150-190^{0}C in the presence of chlorination catalysts. The main application of o-dichlorobenzene is in organic synthesis, in solvents, and in dye manufacture. It is also used in degreasing agents, in wood-preserving compounds, and as a pesticide. p-dichlorobenzene is largely used as a space deodorant and as a moth control agent. The volatile crystals of p-dichlorobenzene have a characteristic penetrating odor. To a lesser extent p-dichlorobenzene is used as a mildew control agent, as an intermediate in the production of dyes, insecticides, pharmaceutical and organic chemicals.

Dichlorobenzenes have been recognized as potential environmental pollutant and are on the EPA list of organic priority pollutants. Calamari et al. (1982) considered p-dichlorobenzene to be of major concern in the atmospheric environment because of the relatively high volatility of the substance. The compound is definitely an environmental contaminant, even if accumulation levels of dichlorobenzene do not appear to be particularly high in various environmental compartments.

Data on specific biodegradation of dichlorobenzenes is limited. In general, dichlorobenzenes can be transformed to chlorophenols. This has been demonstrated in mixed cultures of soil bacteria and by Pseudomonas species (Ballschmiter and Scholz, 1980). Chlorophenols are subject to further degradation and could share the same pathway as 2,4-dichlorophenoxyacetic acid. When dichlorophenols were degraded by microorganisms, halocatechols were found to be the central metabolites and they were subjected to ortho cleavage. Dichlorophenol is more toxic than 2,4-D. Tyler and Finn (1974) found that 25 mg/l of 2,4-dichlorophenol inhibited microbial growth but 2,4-dichlorophenoxyacetic acid at concentrations up to 2 000 mg/l did not. Since dichlorophenol inhibits growth it is only degraded at lower concentrations. A gradual adaptation to degrade dichlorobenzenes increased the biodegradation abilities of microflora which decreased again in subsequent subcultures (Tabak et al., 1981).

As described elsewhere in this report, plasmid transfer has made it possible for a number of microorganisms to use chlorinated hydrocarbons for sole energy and carbon source (Chakrabarty, 1982). This is also evident in dichlorobenzene degradation.

There is a patented duPont process (activated sludge with powdered activated carbon added) available to treat dichlorobenzene pollution (Patterson and Kodukala, 1981). This is less than 40% efficient in different systems.

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CYCLODIENE INSECTICIDES, SELECTED PESTICIDES, AND PERSISTENT COMPOUNDS

The mechanisms that regulate the fate of foreign compounds in soil are both biological and non-biological. Brown (1978) gave a summary of processes influencing herbicides in the soil, but his diagram applies equally well to pesticides and compounds other than herbicides (Fig. 1). The non-biological mechanisms that are of interest here are those that cause the compounds to disappear from the relatively thin upper layer in the soil profile where biological breakdown occurs. The more important of these are leaching and volatilization.

The following compounds have been reviewed:

1 Cyclodiene insecticides

Aldrin		(Fig. 2:1)
Dieldrin		(Fig. 2:2)
Endrin		(Fig. 2:3)
Chlordane		(Fig. 2:4)

2 Halogenated low-carbon compounds

Methylene chloride	(Chlorinated methanes)	(Fig. 4:1)
Chloroform		(Fig. 4:2)
Carbon tetrachloride		(Fig. 4:3)
Trichlorofluoromethane	(Fluorochloromethanes)	(Fig. 4:4)
Dichlorodifluoromethane		(Fig. 4:5)
1,2-dichloroethane	(Chloroethanes)	(Fig. 4:6)
1,1,1-trichloroethane		(Fig. 4:7)
Vinyl chloride	(Chloroethenes)	(Fig. 4:8)
Perchloroethylene		(Fig. 4:9)

3 Phosphonate insecticide

Trichlorfon	(Fig. 5:1)

4 Thiocarbamate herbicide

Triallate	(Fig. 5:2)

1 Cyclodiene insecticides

Insecticides in this group are highly persistent. They remain for several years in soil (Table 1). Estimates of the persistence relate to each compound itself and not to the toxicity, which frequently outlives the parent compound in intermediate metabolites. Aldrin thus has a relatively short half-life in soil but is transformed into dieldrin and persists in this form (Table 1).

The mode of application reflects the respective vapor pressures of the insecticides (Table 1): chlordane and aldrin are added to the soil and dieldrin and endrin to leaves. Use as seed dressing (dieldrin) and use as rodenticide (endrin) are examples of other applications.

Transport of these insecticides or their transformation products can occur through the atmosphere and in erosive runoff (Brown, 1978) but not through leaching of the parent compounds (Freeman et al., 1975; Moza et al., 1972). Hydrophilic breakdown products of the insecticides can both arrive in the ground water (Moza et al., 1972; Kohli et al., 1973) and persist in the soil profile (Stewart and Gaul, 1977).

The target organisms are affected in the synaptic transmission mechanism of the nervous system. Practically insoluble in water, these insecticides are lipophilic and can penetrate skin. They make good contact poisons which can also be ingested or inhaled. Prolonged exposure involves risk of tumours (Table 1).

Aldrin, dieldrin, and endrin contain 85, 83 and 96% (weight of the compound) respectively in typical batches of the technical grade products. Chlorane contains only 43% of the technical grade product, and also heptachlor (Fig. 2:5), a more toxic compound (to ca. 10%) (Brooks, 1974). Improved processing yields a technical grade of chlordane of 95% purity (Stetter, 1983).

Degradation of these compounds occurs biologically as well as through non-biological means. These latter means consist mainly of oxidizing (GÄb et al., 1974), reducing (Butler et al., 1981) agents and γ- (Vollner and Korte, 1974) and UV-irradiation (GÄb, Parlar, and Korte, 1974). Short wavelengths of light seem to cause photoisomerization of either the insecticides themselves or their metabolites (Matsumura, 1982).

Aldrin appears to be the cyclodiene compound that is easiest metabolized by the soil microflora, although non-biological processes might participate in its rather rapid disappearence from the soil profile (Table 1). Apparently the ability to metabolize aldrin is not uncommon among soil microorganisms, as roughly 60 out of 90 isolates were shown to have this ability (Tu et al., 1968). The most effective were isolates of the actinomycetes Nocardia and Streptomyces and of the fungi Trichoderma, Fusarium, and Penicillium.

The major metabolite of aldrin is dieldrin, the epoxide of aldrin. Apparently the soil microflora exclusively form the exo-isomer of dieldrin, as was found by Ferguson and Korte (1977) in tests with 22 strains including Bacillus, Pseudomonas, Micromonospora, Mycobacteria, Nocardia, Streptomyces, and Thermoactinomyces.

Among the cyclodiene compounds dieldrin has been the main target for biodegradation research. The ability to degrade dieldrin, however, is not common. Out of 577 isolates of soil microorganisms only 10 (Pseudomonas, Bacillus, and Trichoderma) were shown to degrade dieldrin, mainly to transdihydroxidihydroaldrin (Fig. 2:1C) (Matsumura and Boush, 1967). Less than 6% dieldrin was degraded by any of these microorganism.

Other dieldrin conversions have been reported for:

Aerobacter aerogenes 12% degradation to transdihydroxidihydroaldrin (Fig. 2:10) (Wedemeyer, 1968).

Trichoderma viride to 41% lipophilic and 2% hydrophilic products (Matsumura and Boush, 1968).

Mucor alternans 26% degradation within two days (Anderson et al., 1970).

One metabolite, photodieldrin (Fig. 2:6), known to be a photoisomerization product, is also formed from dieldrin by the soil microflora (Matsumura et al., 1970). Photodieldrin is considered more toxic than dieldrin but can be degraded further. Three hydrophilic metabolites, notably the bridged isomers of transdihydroxidihydroaldrin and dihydrochlordene dicarboxylic acid (Fig. 2:12 and 9), were shown to be formed in ^{14}C-photodieldrin treated soil (Weisgerber et al., 1975). The expected ketone (Fig. 2:8), known from insect and probably mammalian metabolism, was not found in this investigation.

Another degradation of ^{14}C-photodieldrin was conducted with the soil fungus Trichoderma viride. The initial insecticide concentration was 1 ppm and between 32 and 41% of water soluble compounds from the degradation were formed over 4 - 5 weeks time. The water-soluble products were bioassayed on mosquito larvae and found to be harmless. A loss of tracer activity during the incubation was attributed to volatilization of break-down products, of which carbon dioxide was suspected to be one (Tabet and Lichtenstein, 1976).

The degradation of chlorinated, cyclic, dieldrin-carbon to carbon dioxide (involving ring cleavage) has been reported for isolates of Trichoderma koningi (Bixby et al., 1971) and for soil samples, as well as isolates (3 strains) of bacteria (Jagnow and Haider, 1972). T. koningi evolved 3.1% of the initial insecticide-^{14}C-activity as ^{14}C-carbon dioxide in

17 days. The soil samples gave 1.86% ^{14}C-carbon dioxide over 7 weeks from an initial 10 ppm of insecticide, and the most potent isolate (Micrococcus 265) released 0.2% ^{14}C-carbon dioxide over 5 weeks from initially 0.4 ppm dieldrin.

Although the overall process seems to be slow, this shows that there is at least a partial mineralization of aldrin/dieldrin in soil. A picture of the breakdown pathways is emerging (Fig. 3) (Matsumura and Benezet, 1978). Known degradation products from soil include ketone, aldehyde, alcohol, and acid compounds as well as photoisomers of some of these (Matsumura et al., 1968; Vockel and Korte, 1974; Scheunert et al., 1977). Of these only the dichlordene dicarboxylic acid was shown to suffer (an unchlorinated) ring cleavage (Fig. 2:7).

Endrin (Fig. 2:3) is an isomer of dieldrin. Of twenty dieldrin degrading strains all were capable of degrading endrin (Patil et al., 1970). Of these strains 12 belonged to Pseudomonas and Bacillus, 2 were Trichoderma viride, and one was Micrococcus, one Arthrobacter and 4 unidentified. On the other hand, only 25 out of 150 soil isolates were able to degrade endrin in another investigation (Matsumura et al., 1971).

In flooded soils biodegradation was more rapid under anaerobic than under aerated conditions (Gowda and Sethunathan, 1977). Degradation was also more rapid in soils with a higher content of organic matter. A non-biological reduction, which occurred when zinc was added to the soil, gave a high degree of endrin degradation (Butler et al., 1981). Preliminary tests with alternating anaerobic-aerobic biodegradation were unsuccessful (Gowda and Sethunathan, 1977).

More than six degradation products were found in the above investigations, with keto-endrin (Fig. 2:11) the one most often identified (Matsumura

et al., 1971). The disappearance rate of endrin from flooded soils under the most successful conditions was over 90% during 55 days from initially ca. 25 ppm (Gowda and Sethunathan, 1976). The authors, however, carefully underline that this was not a complete degradation and that the metabolites formed appeared to be more persistent than endrin itself. Moreover, the toxicity of the metabolites remained untested (Gowda and Sethunathan, 1977).

Chlordane (Fig. 2:4) is considered to have a half-life of 1.0 years and so would be one of the least persistent of the cyclodiene pesticides listed. Still, it can persist in certain conditions for 15 years in the soil (Table 1).

In laboratory cultures Aspergillus niger utilized chlordane completely over 48 hours from an initial concentration of 12.5 ppm and to 87.5% from initially 50 ppm. Growth of A. niger was enhanced relative to the control with a maximum at 37.5 ppm pesticide, and inhibition occurred at concentrations over 50 ppm. Chlordane adaptation more than doubled the rate of oxidation of chlordane, heptachlor, and aldrin (Iyengar and Rao, 1973).

Of the cyclodiene compounds surveyed here most of the work has been done on the degradation of the aldrin/dieldrin group. The efforts until now, however, have failed to give the knowledge needed to design a process that is able to deal with accumulations of these compounds in the environment. The difficulties often lie in low turn-over rates. The ability to tolerate higher concentrations of the pesticides is another characteristic that is often lacking and, further, most of the experiments have been carried out in batch cultures, thus leaving the problem of creating a system that is able to operate continually. The situation is about the same for endrin and chlordane.

2 Halogenated low-carbon compounds (Fig. 4)

These compounds are rather soluble in water and share high vapor pressures (Table 2). Volatilization is considered to be important (Treatability.., 1980), and in most cases to predominate over sorption and biodegradation.

In recent years interest in biodegradation has increased. A screening of organic priority pollutants in aqueous culture with microbial inoculae obtained from settled domestic wastewater indicated a biodegradation of six of the compounds listed here (Tabak et al., 1981). These results are listed in Table 3. An increase of degradability in subcultures (columns "1st" - "3rd") indicates adaptation in the microbial communities towards the compound in question.

On the other hand, to enrich and isolate pure strains of bacteria, with the purpose of degrading certain compounds, is more difficult. Stucki et al. (1981) attempted enrichment from 33 different soil and sewage samples, 22 of which were from sites previously exposed to chlorinated hydrocarbons. All compounds listed here, except dichlorodifluoromethane and vinyl chloride, were among those tested, but only two pure cultures were obtained, one of them degraded methylene chloride. Two enrichment cultures were obtained that degraded 1,2-dichloroethane.

Of the chloromethanes, chloroform (Fig. 4:2) and carbon tetrachloride (Fig. 4:3) have increasingly come to be used in more contained situations in fluorocarbon production and other industrial processes. (Chloroform, etc., 1978). In the USA, only 5% of the carbon tetrachloride and 7% of the chloroform produced in 1973 were used for purposes with a high risk of dispersion (e.g. solvents and fumigants). The use of methylene chloride (Fig. 4:1) varied with a high probability of dispersive uses.

Methylene chloride, in addition to the degradability test by Tabak et al. (1981), has been subjected to degradability tests using both microbial communities and individual strains of microorganisms.

A continuous-flow activated sludge system (Kincannon et al., 1983) was shown to biodegrade methylene chloride to 93%. Most of the compound remaining was lost due to volatilization (air-stripping). Influent and effluent methylene chloride concentrations were 180 and 0.51 mg/l respectively and the flow rate was 6 ml/min.

An essentially steady-state removal of methylene chloride was effected in a fixed-film system with bacteria enriched from sewage (Rittmann and McCarty, 1980). The methylene chloride was used as the sole exogenous energy source. The small reactor, 12 cm long by 2,5 cm in diameter, processed 2 liters influent a day, reducing the methylene chloride concentration from 23.8 ppm to ca 1 ppm.

Bacterial degradation of methylene chloride has been shown for the strains DM 1 and DM 2, the former a Pseudomonas species. DM 1, which introduced itself as an airborne contaminant, showed the highest degradation rate of methylene chloride (0.53 g/liter/hour), and was inhibited by higher methylene chloride concentrations (Brunner et al., 1980). DM 1 also has been adapted to an immobilized-cell system, but with a loss of 75% of the dehalogenating capacity (Stucki et al., 1981). DM 2 was described in the same paper.

Chloroform was degraded in the screening-test mentioned above (Tabak et al., 1981) after an initial period of adaptation. Another aerobic degradation of chloroform was reported for a suspension of soil taken from an area 9 months after a major chloroform spill occurred there (Flathman and Dahlgran, 1982).

Anaerobic degradation of chloroform was obtained in an aqueous medium with seed from waste-activated sludge (Bouwer et al., 1981). These authors were unable to bring about a breakdown of chloroform under aerobic conditions.

In reports on the behaviour of chloroform in soils, it is found to pass quite rapidly through the profile (Bouwer, McCarty et al., 1981) with retardation factors of 1.5 times that of interstitial water (Wilson et al., 1981). This passage is so rapid that the compound might pass the biologically active zone without degradation (Rittmann et al., 1980). Contrary to this the chloroform content of the soil 9 months after the aforementioned spill (Flathman and Dahlgran, 1982) was 490 mg/l.

Considering the short time that interest has been focused on chloroform degradation, it is not surprising to find divergent observations. It also seems that chloroform is rather mobile and has to be "trapped" to obtain a degradation.

Carbon tetrachloride is considered to be the most toxic of the chloromethanes. It also is a volatile compound, but appears to be rather easily biodegraded, provided it can be kept in a suitable environment for the time required (Tabak et al., 1981).

The fluorochloromethanes considered here, trichlorofluoromethane and dichlorodifluoromethane are highly volatile and not biodegradable (Treatability.., 1980; Tabak et al., 1981; Wakeham et al., 1983).

Chloroethanes tend to be volatilized (stripped) from degrading experiment containers (Kincannon et al., 1983): 1,2-dichloroethane to 99% and 1,1,1-trichloroethane to 100%. These compounds are not degraded or only degraded in small amounts: a microbial commuity was shown to degrade 1,2-dichloroethane (Stucki et al., 1981) and Tabak et al. (1981) (Table 3) re-

ported a slow to moderate degradation of both compounds. 1,2-dichloroethane was found to percolate rapidly through soil (Wilson et al., 1981).

Of the chloroethylenes, perchloroethylene in artificial aquifer tests did not disperse very far from the point of injection (ca. 20 m), apparently due to a combination of adsorption and volatilization (Betz et al., 1983). For sandy soils with a low content of organic matter, a rather fast transport was found into the underlying ground water. Perchloroethylene here behaved similarly to chloroform and 1,2-dichloroethane (Wilson et al., 1981).

Biodegradation of perchloroethylene was shown by the screening test of Tabak et al. (1981), although biodegradation in nature probably is rendered of secondary importance for this compound, as well as for vinyl chloride (Treatability.., 1980). No reference to biodegradation of vinyl chloride was found in our survey.

Of the low-carbon halogenated compounds many are easily volatilized and so tend to eliminate themselves rather rapidly after application to soil. The fluorochloromethanes obviously behave in this way. Chloroform, 1,2-dichloroethane, and perchloroethylene have been shown to penetrate certain soils to the ground water. These compounds are biodegradable after adaptation except for 1,2-dichloroethane, which is only slowly to moderately degradable.

The compound for which degradation research is most advanced is methylene chloride. For this compound the best degrading systems appear ready for practical tests.

3 Phosphonate insecticide

Trichlorfon is one of the least toxic organophosphorous insecticides and also is not persistent (Brown, 1978).

The information on biodegradation of the compound is scarce (Treatability..., 1980). Enrichment cultures utilizing organophosphorous pesticides, including trichlorfon, were readily obtained, and trichlorfon was found to be used as a sole source of phosphorous by a bacterial isolate (Rosenberg and Alexander, 1979). The trichlorfon, however, was not used as a sole source of carbon.

The breakdown of trichlorfon appears to be, partly at least, exoenzymatic (Molozhanova et al., 1973: from Matsumura and Benezet, 1978) and is carried out by Penicillium cyclopium, Aspergillus niger, Mucor mucedo, Trichoderma viride, and Actinomyces griseus.

Hydrolysis is given as one pathway in the biodegradation by Zayed et al. (1965) who worked with Aspergillus, Penicillium, and Fusarium (Fig. 5:1).

4 Thiocarbamate herbicide

Triallate is a thiocarbamate herbicide, that is used in early season control and is applied both before and after emergence. Its relatively low toxicity is demonstrated by an oral LD_{50} of 1,471 mg/kg for rats (Registry..., 1982).

Triallate is not considered to be persistent (Brown, 1978), but application to soils can result in a carry-over from one season to the next with the residual fractions making up 10 - 29% of the applied amount in years with high precipitation and 42 - 98% in years with low precipitation. The higher percentages result from a less volatile formulation (Smith and Hayden, 1981).

The compound is lost from soil along three main routes: biodegradation, bound residue formation, and volatilization. This was shown in experiments with ^{14}C-labelled triallate over 52 weeks in a closed system soil incubator. The loss of herbicide was found to be concentration-dependent with a maximum at 1 ppm. Of the recovered radioactivity 4.4% was atmospheric triallate and 56.2% $^{14}CO_2$. From soil 13.8% was recovered as triallate and 23.6% was unextractable (Anderson and Domsch, 1980).

In another series of experiments, it was demonstrated that the soil water content influenced the rates of volatilization, degradation, and binding of triallate. The highest soil water content (19%) gave the lowest values for triallate: 4.3% in the atmosphere, 20.8% in the soil, 17.5% $^{14}CO_2$, and 55.2% unextractable in the soil (Anderson, 1981) over 10 weeks time.

The work referred to above, including field measurements (Smith and Hayden, 1981) and laboratory soil incubator tests (Anderson and Domsch, 1980; Anderson, 1981), indicates rather brief persistence in soil.

Neither the microorganisms participating in the degradation of triallate, nor the degradation pathways have been described.

There is, however, a compilation of a probable pathway, that has been assembled from available data, mainly from animal and plant physiology (Fig. 5:3) (Fang, 1975).

Table 1 Properties of cyclodiene insecticides.

Insecticide	Vapor pressure mm Hg; 25°C	Toxicity, mg/kg LD_{50} orl, rat	Carcino-genicity	Persistence years	Half-life years	95% disappearence years
Aldrin	6×10^{-6}	67	+	15	0.3	3
Dieldrin	1.8×10^{-7}	40 - 87	+	15	2.5	8
Endrin	2×10^{-7}	7,5 - 17,5	susp.	14	2.2	7
Chlordane	1×10^{-5}	283 - 590	+	15	1.0	4
Heptachlor	4×10^{-4}	90 - 135	+	—	0.8	3.5
Source	Stetter, 1983	Stetter, 1983	Registry of toxic eff., 1982	Saxena and Chakrabarti, 1979	Brown, 1978	Brown, 1978

Table 2 Properties of 1- and 2-carbon halogenated compounds.

Compound	Water solubility mg/l	Vapor pressure mm Hg; 20°C	Toxicity, mg/kg LD_{50} orl, rat	carcinogenicity (x)
Methylene chloride	16,700 (25°C)	362	167	?
Chloroform	9,600 (20°C)	120	800	A, H?
Carbon tetrachloride	800 (20°C)	90	2,800	A, H?
1,2-dichloroethane	8,300 (20°C)	61	670	A H?
1,1,1-trichloroethane	950 (20°C)	96	10,300	?
Vinyl chloride	1.1 (25°C)	2,660 (25°C)	500	H
Perchlorethylene	150 (20°C)	14	8,850	A
Trichlorofluoromethane	1,100	667	10xx)	?
Dichlorodifluoromethane	280 (25°C)	4,310	76xx)	-
Source	Treatability manual 1, 1980		Registry of toxic effects, 1982	

x) A-carcinogenic in test animals; H-carcinogenicity in humans; ?-carcinogenicity suspected

xx) values refer to LC_{50} ihl, mouse

Table 3 Biodegradability and volatility studies with halogenated aliphatics evaluated by the static-screening-flask test method. (From Tabak et al., 1981).

Test compound	Conc. (mg/l)	Performance summary	Average total loss of test compound in 7 days incubation time (%)				Volatilization loss (%)	
			Original	First	Second	Third	5° C	25° C
Chloroethanes								
1,1-Dichloroethane	5	B	26	41	54	63	0	27
	10	B	20	35	51	53	0	5
1,1,1-Trichloroethane	5	B	29	64	76	83	0	27
	10	B	23	53	68	75	0	7
Halomethanes								
Methylene chloride	5	D	100	100	100	100	0	25
	10	D	100	100	100	100	0	6
Carbon tetrachloride	5	D	87	100	100	100	0	23
	10	D	80	100	100	100	0	5
Chloroform	5	A	49	85	92	100	0	24
	10	A	46	70	80	100	0	6
Trichlorofluoromethane	5	N	59	61	65	73	5	58
	10	N	38	40	43	45	2	37
Chloroethylenes								
Tetrachloroethylene	5	A	45	54	69	87	0	23
	10	A	30	41	67	89	0	16

D - Significant degradation with rapid adaptation
A - Significant degradation with gradual adaptation
B - Slow to moderate biodegradative activity, concomitant with significant rate of volatilization
N - Not significantly degraded under the conditions of test method and/or precluded by extensive rate of volatilization

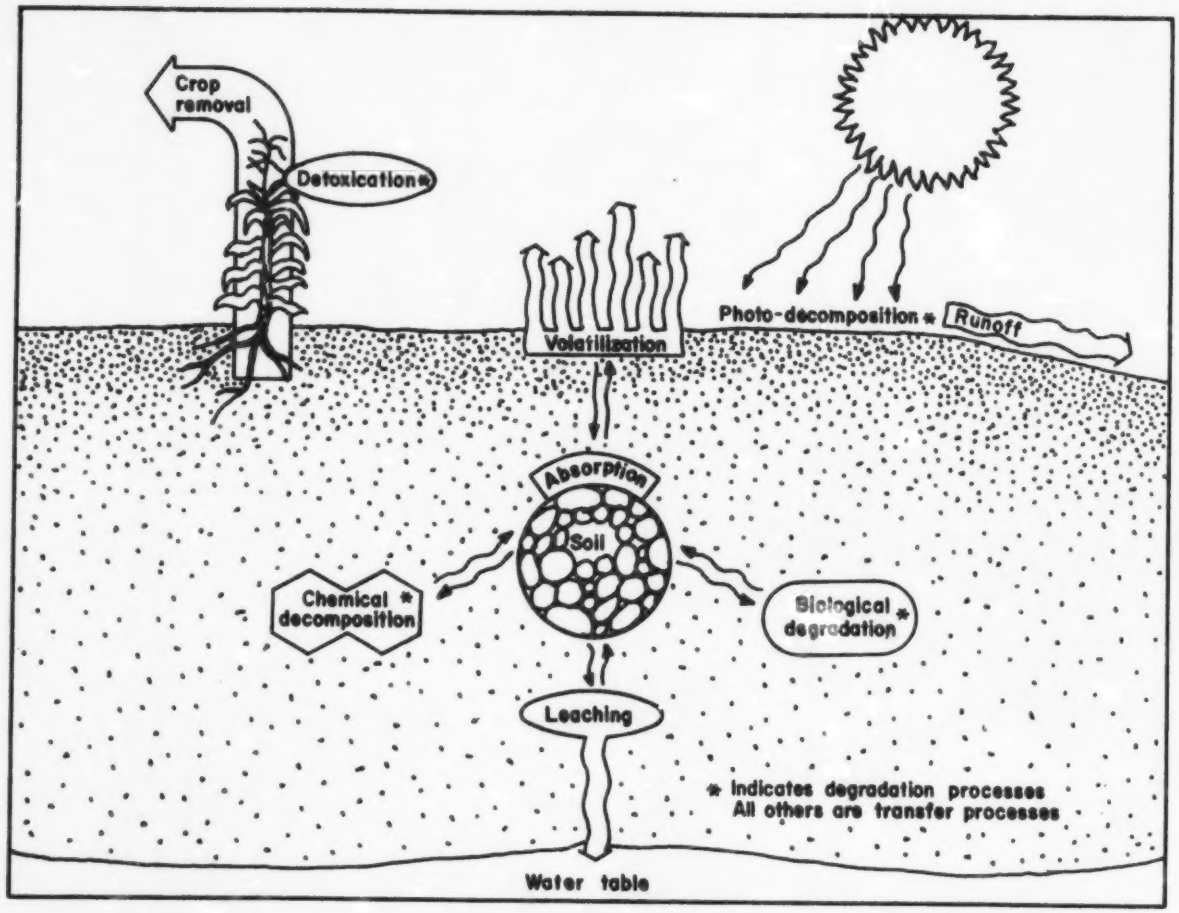
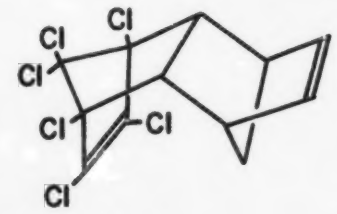
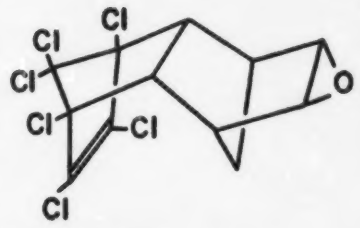


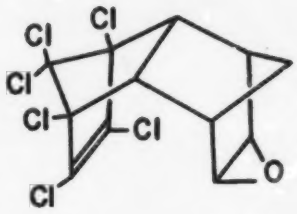
Fig. 1. Processes influencing the behaviour and fate of foreign compounds in the soil. (After Brown, 1978).



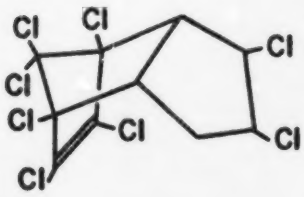
(1) aldrin



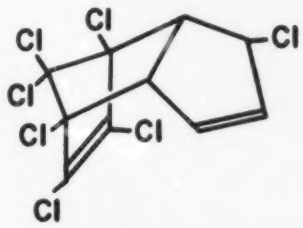
(2) dieldrin



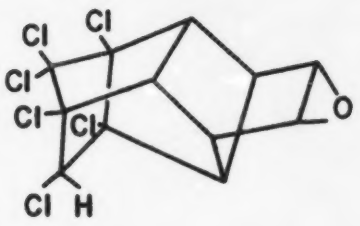
(3) endrin



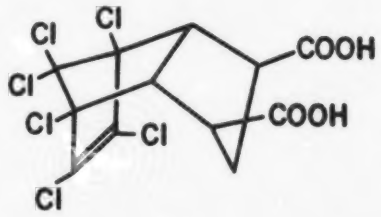
(4) chlordane



(5) heptachlor



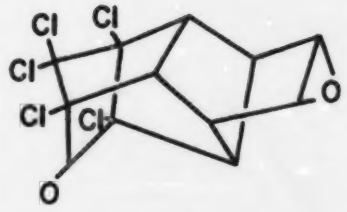
(6) photodieldrin



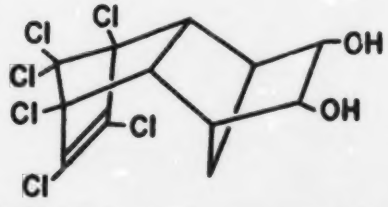
(7) dihydrochlordene dicarboxylic acid

Fig. 2. Structures of chlorinated cyclodienes and some of their metabolites.

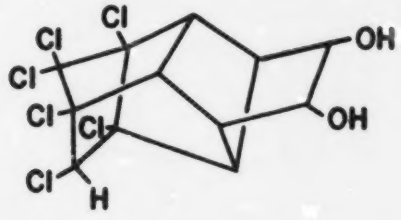
(Continued on next page).



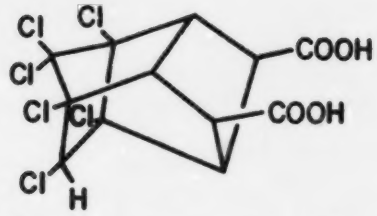
(8) Pentachloroketone metabolite



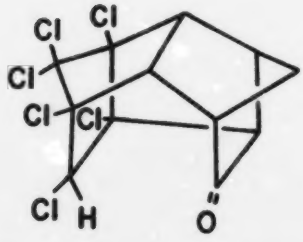
(10) Trans-dihydroxidihydroaldrin
Trans-aldrindiol



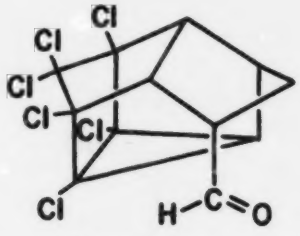
(12) Bridged isomer of trans-dihydroxidihydroaldrin



(9) Bridged isomer of dihydrochlordene dicarboxylic acid



(11) "Half-cage ketone"



(13) "Pentacyclic aldehyde"

Fig. 2. (Continued).

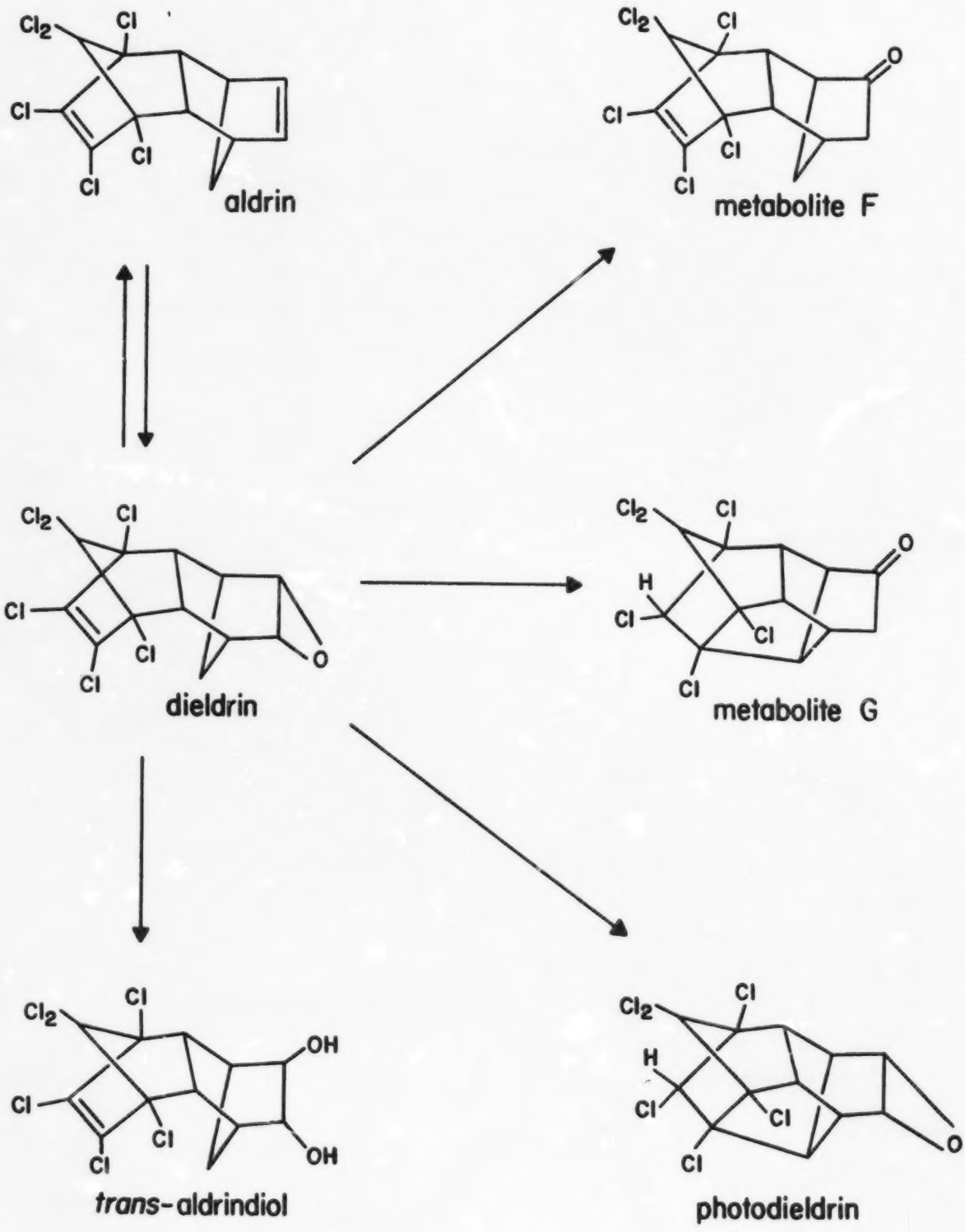


Fig. 3. Pathways of dieldrin and aldrin transformations by microorganisms. (After Matsumura and Benezet, 1978).

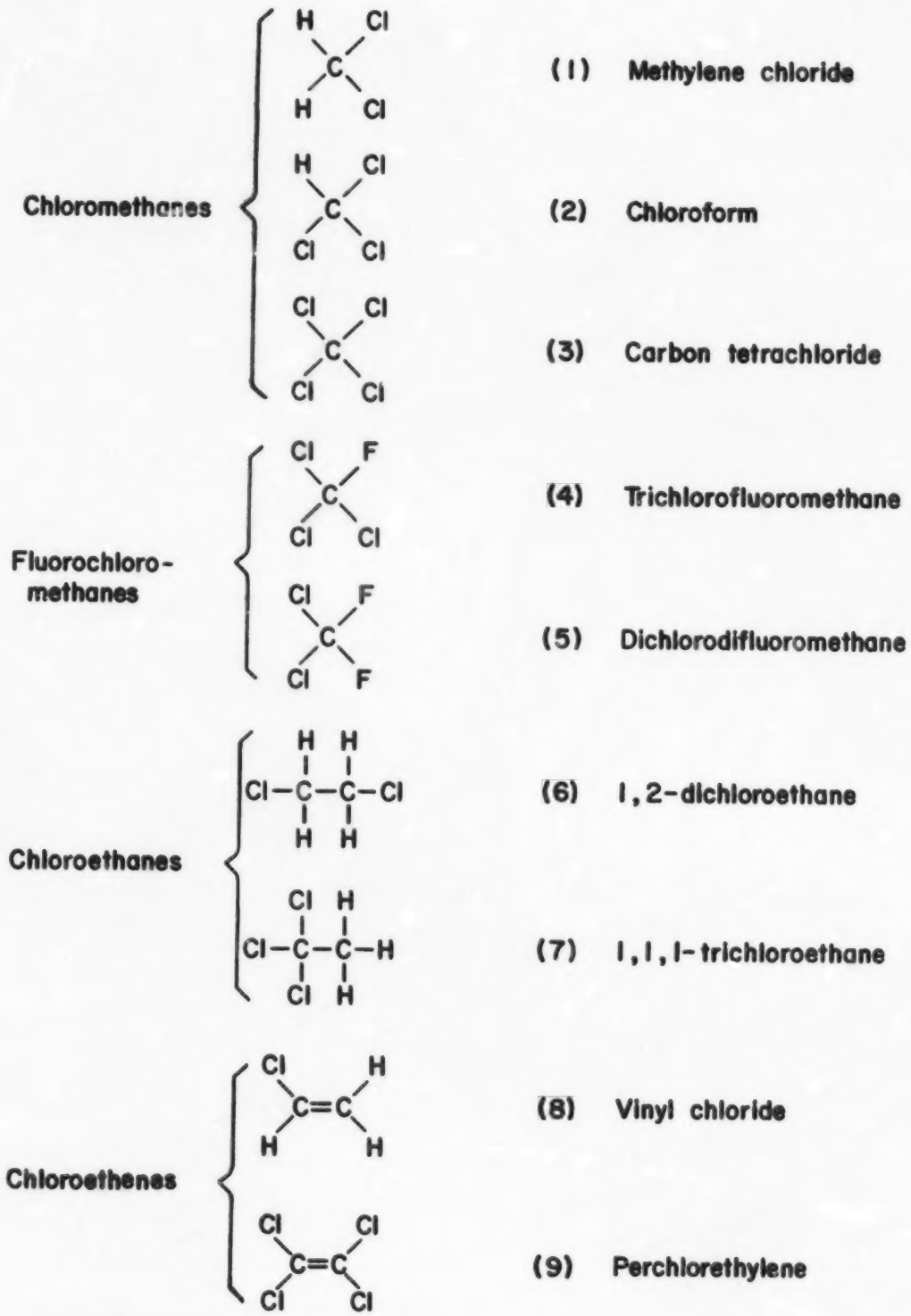
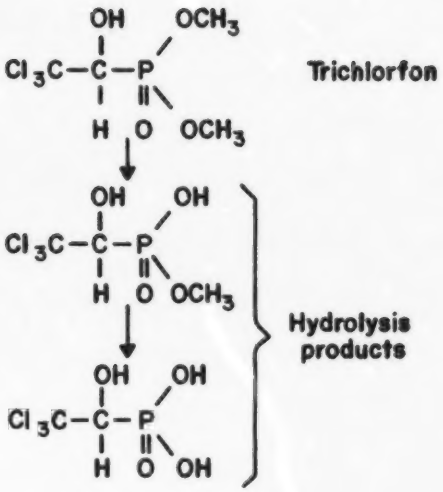
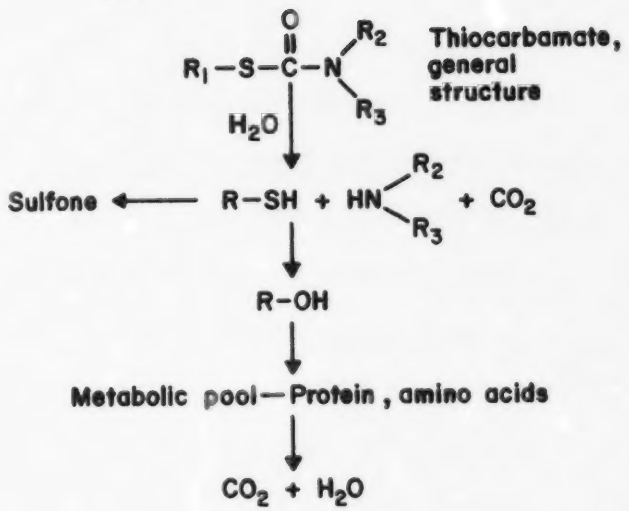


Fig. 4. Structures of 1- and 2-carbon halogenated compounds.

(1)



(3)



(2)

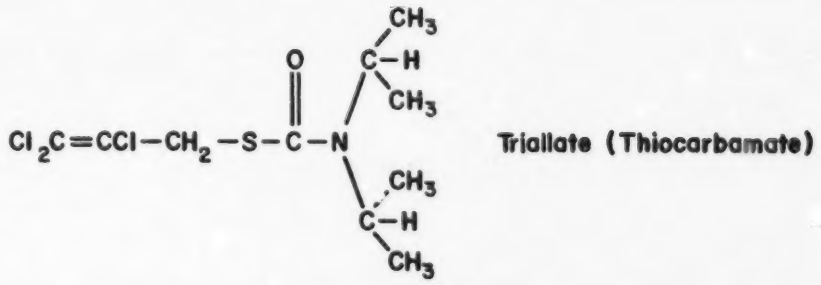


Fig. 5. Structures and suggested metabolic pathways of trichlorfon and triallate. ((1) After Zayed et al., 1965. (2) After Fang, 1975).

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